<Division of Environmental Chemistry>Hydrospheric Environment Analytical Chemistry

Division of Environmental Chemistry
– Hydrospheric Environment Analytical Chemistry –

http://inter3.kuicr.kyoto-u.ac.jp/scope_E.html

Prof
SOHRIN, Yoshiki
(D Sc)

Assoc Prof
UMETANI, Shigeo
(D Sc)

Techn Staff
MINAMI, Tomoharu
(D Eng)

Students

TAKANO, Shotaro (D3)
ZHENG, Linjie (M2)
MURATA, Rena (M1)
SASAKI, Masanobu (M1)

Scope of Research

(i) Biogeochemistry of trace elements in the hydrosphere: Novel analytical methods are developed for trace metals and their isotopes. Distribution of trace elements in the hydrosphere and their effects on ecosystem are investigated. The study also covers hydrothermal activity, deep biosphere and paleocean.
(ii) Ion recognition: Novel ligands and ion recognition system are designed, synthesized and characterized.

KEYWORDS

Marine Chemistry
Analytical Chemistry
Trace Elements
Stable Isotopes
Metal Ion Recognition

Selected Publications

Takano, S.; Tanimizu, M.; Hirata, T.; Sohrin, Y., Isotopic Constraints on Biogeochemical Cycling of Copper in the Ocean, *Nat. Commun*., **5,** doi:10.1038/ncomms6663 (2014).
Nägler, T. F.; Anbar, A. D.; Archer, C.; Goldberg, T.; Gordon, G. W.; Greber, N. D.; Siebert, C.; Sohrin, Y.; Vance, D., Proposal for an International Molybdenum Isotope Measurement Standard and Data Representation, *Geostand. Geoanal. Res*., **38**, 149-151 (2014).
Takano, S.; Tanimizu, M.; Hirata, T.; Sohrin, Y., Determination of Isotopic Composition of Dissolved Copper in Seawater by Multi-collector Inductively Coupled Plasma Mass Spectrometry after Pre-concentration Using an Ethylenediaminetriacetic Acid Chelating Resin, *Anal. Chim. Acta*, **784,** 33-41 (2013).
Vu, H. T. D.; Sohrin, Y., Diverse Stoichiometry of Dissolved Trace Metals in the Indian Ocean, *Sci. Rep*., **3,** doi: 10.1038/srep01745 (2013).
Cid, A. P.; Nakatsuka, S.; Sohrin, Y., Stoichiometry among Bioactive Trace Metals in the Chukchi and Beaufort Seas, *J. Oceanogr*., **68,** 985-1001 (2012).
Firdaus, M. L.; Minami, T.; Norisuye, K.; Sohrin, Y., Strong Elemental Fractionation of Zr-Hf and Nb-Ta across the Pacific Ocean, *Nature Geosci*., **4,** 227-230 (2011).

Biogeochemical Cycling of Copper Isotopes in the Ocean

Copper plays an important role as a micronutrient for organisms, but it is also toxic at high concentrations of the free Cu^{2+}. In the ocean, Cu is subjected to various biogeochemical processes, such as atmospheric input, biological uptake, and adsorption onto sinking particles. Precise isotopic measurement of Cu has become possible since the advent of multiple collector inductively coupled plasma mass spectrometry. To elucidate the biogeochemical cycling of Cu in the oceans, it is important to determine the profiles of Cu isotopes in the ocean, because Cu isotopes are fractionated during various biogeochemical processes. We have determined dissolved Cu concentration and the isotopic composition of seawater samples collected from the western/eastern North Pacific, the central South Indian, and the North Atlantic. The isotopic composition is reported as $\delta^{65}Cu=[(^{65}Cu/^{63}Cu)_{sample}/(^{65}Cu/^{63}Cu)_{NIST\ SRM\ 976\ standard}-1]\times10^3$. Observed $\delta^{65}Cu$ is from +0.41 to +0.48‰ in the surface seawater and becomes heavier in the depths. In the deep seawater, $\delta^{65}Cu$ ranges from +0.41 to +0.85‰ and correlates with AOU that is a measure of the age of deep seawater. We propose that $\delta^{65}Cu$ in surface seawater is a mixture of rain water, river water, and deep seawater, and $\delta^{65}Cu$ in deep seawater becomes heavier with the age of deep seawater because of preferential removal of light Cu isotopes. Also, we build a new box model for Cu in the ocean based on the combination of Cu concentration and $\delta^{65}Cu$, which successfully constrains marine biogeochemical cycling of Cu (Figure 1).

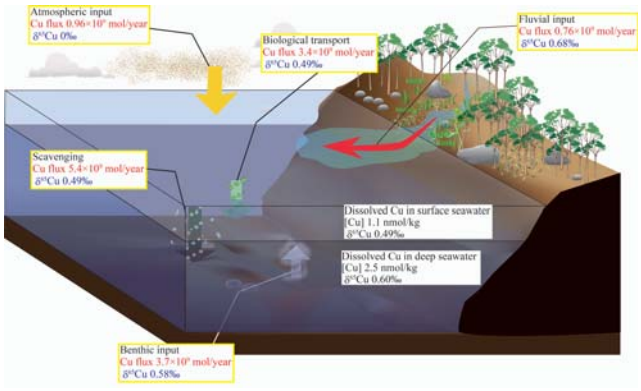

Figure 1. Box model for Cu cycling in the ocean based on both elemental concentration and isotopic ratio.

An Off-line Automated Preconcentration System with Ethylenediaminetriacetate Chelating Resin for the Determination of Trace Metals in Seawater by High-resolution Inductively Coupled Plasma Mass Spectrometry

Trace elements and their isotopes (TEIs) in the ocean are important as tracers in oceanography, micronutrients and/or toxins in biogeochemistry, and proxies in paleoceanography. Recently, an international research program of the marine biogeochemical cycles of TEIs, referred to as GEOTRACES, was commenced to determine the distributions of key TEIs (such as Al, Mn, Fe, Cu, Zn, Cd, and Pb) and to clarify their sensitivity toward changing environmental conditions. While high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) is a powerful technique in the multi-elemental determination of trace metals, major constituents of seawater interfere with the precise determination. A novel automated off-line preconcentration system for trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) in seawater was developed by improving a commercially available solid-phase extraction system SPE-100 (Hiranuma Sangyo). The utilized chelating resin was NOBIAS Chelate-PA1 (Hitachi High-Technologies) with ethylenediaminetriacetic acid and iminodiacetic acid functional groups. Parts of an 8-way valve made of alumina and zirconia in the original SPE-100 system were replaced with parts made of polychlorotrifluoroethylene in order to reduce contamination of trace metals. The eluent pass was altered for the back flush elution of trace metals. We optimized the cleaning procedures for the chelating resin column and flow lines of the preconcentration system, and developed a preconcentration procedure, which required less labor and led to a superior performance compared to manual preconcentration. The nine trace metals were simultaneously and quantitatively preconcentrated from ~120 g of seawater, eluted with ~15 g of 1 M HNO_3, and determined by HR-ICP-MS using the calibration curve method. The single-step preconcentration removed more than 99.998% of Na, K, Mg, Ca, and Sr from seawater. The procedural blanks and detection limits were lower than the lowest concentrations in seawater for Mn, Ni, Cu, and Pb, while they were as low as the lowest concentrations in seawater for Al, Fe, Co, Zn, and Cd. The accuracy and precision of this method were confirmed by the analysis of reference seawater samples and seawater samples for vertical distribution in the western North Pacific Ocean.